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A Molecular Theory of Detonation Velocity in Gaseous and Solid Explosives*

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It is assumed that the rate determining step in detonation of gaseous and solid explosives is the rate of transference of activation energy which can be supplied by reactant molecules translating with a part of the heat energy of combustion.

I. Thus, the velocity (V_G) of detonation wave can be expressed by the relation as follows:

$$\frac{1}{2}MV_G^2 = JQ \frac{f_t}{F} + \frac{1}{2}f_tRT \quad (1)$$

where M is the total mass of reactant molecules of elementary reaction, J the mechanical equivalent of heat, f_t the degree of freedom of translation, F the total degree of freedom of the reactants, R the gas constant and T the absolute temperature of the experiment.

II. Inert gas effect on detonation velocity can be given by analogous relation to Eq. (1), assuming that even polyatomic gas molecules behave as monatomic in the duration of collision.

III. Further, the detonation velocity (V_S) of solid explosives are expressed by the relation as follows:

$$V_S = V_G(v/v_f)^{1/3} \quad (2)$$

where V_G is the same as defined by Eq. (1), v the molecular volume of the solid explosives and v_f the free volume of them. The relation (2) is used after the analogy of the relation between the propagation velocities of sonic wave in gas and liquid.

Observed values available in the literature show good agreement with the calculated ones given by the theory, I, II and III respectively.

INTRODUCTION

Propagation is one of the fundamental characteristics of combustion phenomena and has been investigated for a long time from various points of view experimentally and theoretically. Especially, detonation is an extraordinary phenomenon in combustion and has been discussed in the main hydrodynamically.^{1,2)} The hydrodynamical theory is purely mechanical, and it is in most respects a satisfying theory from the

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physical point of view. But, as J.Taylor²⁾ pointed out, it is less satisfactory from the chemical point of view, and it can not predict the detonation velocity from the chemical constitution or chemical nature of the explosives.

The present authors previously proposed a simple theory of limits of inflammability as a limiting condition for flame propagation.³⁾ In that theory, it was assumed that the propagation of a flame can be carried out by the energy released at the flame front, which is transported by the reactant and excess molecules around as the kinetic energy of such molecules. The condition for both ignition and propagation was given by the relation,

$$\alpha(Q+E)/E \gg 1, \quad (1)$$

where α is the efficiency coefficient of activation, Q the heat of combustion, and E the activation energy. In this report, it will be shown that the propagation velocities of detonation in gaseous and solid explosives can be represented by mean velocity of translation of the reactant molecules which may reserve the reaction heat as their kinetic energy.

I. Detonation Velocity in Gases

It is very complicate to discuss the propagation velocity of a flame in explosive gas mixtures, because it is generally accompanied by thermal and hydrodynamical confusion. But then detonating flame, whose velocity is comparable with or larger than the sonic wave, may be considered to be free from such confusion. In other words, the detonation wave seems macroscopically to propagate through the explosive gas mixture at rest and it may be treated simply as a secondary activation process in rapid succession. In the case of detonation, the condition given by the relation (1) must be fully satisfied with respect to the concentration and energy. Since atomic rearrangement or reaction itself must be extraordinarily rapid, the propagation velocity may be determined mainly by the rate of activation or the rate of transportation of the activation energy. It may be presumed that only the most efficient process of activation needs to be considered as far as detonation is concerned, though some delayed or less efficient reaction may follow the detonation wave. Assuming that the activation is carried out by the reactant molecules for which the heat of combustion should be delivered, propagation velocity of detonation wave may be represented by the mean velocity of the translation of the reactant molecules.

Berthelot-Vieille (1882)⁴⁾ and Dixon (1803)⁵⁾ assumed that the detonation velocity could be given by the mean translation velocity (V) of the molecules at the temperature (T) of the flame and gave the relation,

$$\frac{1}{2} \cdot M V^2 = \frac{3}{2} \cdot \frac{RT}{N}, \quad (2)$$

where M is the molecular weight of the reactant, N the Avogadro's constant, and

R the gas constant. They regarded the reactant molecules as monatomic, but it is not proper for the case. Bernard Lewis¹⁾ once proposed a theory of detonation in which he assumed that the energy liberated in the elementary reaction of chain mechanisms was distributed equally among every degree of freedom of the reactant molecules of atoms and that the maximum energy of them gave the velocity of detonation. But generally it is very difficult to ascertain the chain mechanism.

Now, we propose a simpler theory of detonation in a modified form of the theory of Berthelot-Vieille and B. Lewis. It is assumed that the energy liberated at the flame front of detonation is distributed equally among all the degree of freedom of the reactant molecules and that only the energy of translation can contribute to the velocity of translation. Taking a single stoichiometric reaction as the unit of reaction, we have

Table 1. Propagation velocity of detonation wave in gas mixture.

Reactions	M	Q Kcal	Q/M	f_t	f_v	f_r	F	f_t/F	V_{calc} m/sec	V_{obs}^* m/sec
1. $H_2 + \frac{1}{2}O_2 = H_2O$	18	58	3.11	3	6	3	12	0.25	2663	2819
2. $H_2 + Cl_2 = 2HCl$	72	44	0.61	6	4	4	14	(0.43)	1548	1730
3. $CO + \frac{1}{2}O_2 = CO_2$	44	68	1.54	3	8	2	13	0.23	1775	$\begin{cases} 1680^{**} \\ 1264 \end{cases}$
4. $C_2N_2 + 2O_2 = 2CO_2 + N_2$	116	258	2.22	9	18	6	33	0.27	2296	2321
5. $CH_2 + 2O_2 = CO_2 + 2H_2O$	80	218	2.73	9	20	8	37	0.24	2414	2322
6. $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	124	323	2.60	12	28	10	50	0.24	2339	2368
7. $C_2H_2 + \frac{5}{2}O_2 = 2CO_2 + H_2O$	106	312	2.95	9	22	7	38	0.24	2458	2391
8. $2NH_3 + \frac{3}{2}O_2 = N_2 + 3H_2O$	41	83	2.02	6	10	5.5	21.5	0.27	2256	2390
9. $C_2H_6 + \frac{7}{2}O_2 = 2CO_2 + 3H_2O$	142	372	2.61	15	34	13	62	0.24	2359	2363
10. $CS_2 + 3O_2 = CO_2 + 2SO_2$	172	265	1.54	9	24	6	39	0.23	1762	1800
11. $C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$	204	485	2.36	21	48	18	87	0.24	2249	2280
12. $C_4H_{10} + \frac{13}{2}O_2 = 4CO_2 + 5H_2O$	266	934	2.38	27	62	23	112	0.24	2249	2270
13. $C_5H_{10} + 8O_2 = 5CO_2 + 6H_2O$	328	780	2.40	33	76	28	137	0.24	2245	2371
14. $C_6H_6 + \frac{15}{2}O_2 = 6CO_2 + 3H_2O$	318	750	2.35	27	66	21	114	0.24	2210	2206
15. $C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$	142	438	3.08	15	34	13	62	0.24	2540	2356

* Lewis and von Elbe: "Combustion, Flames and Explosions of Gases," 1951, p. 583-609.

** Dixon: Phil. Trans. Roy. Soc. A 184, 97 (1893). Stettbacher: "Schiess- u. Sprengstoff," 1933, p.62

$$\frac{1}{2} M V_g^2 = J(f_t/F)(Q+E) + f_t RT/2, \quad (3)$$

where M is the total mass of the reactant molecules. V_g the mean velocity of them, J the mechanical equivalent of heat, Q the heat of reaction, E the energy of activation, f_t the degree of freedom of translation of the reactant molecules, F the total degree of freedom of the reactant molecules,* R the gas constant and T the absolute temperature of the experiment. $RT/2$ represents the kinetic energy per one degree of freedom at T . Granting that V_g corresponds to the detonation velocity and E can be neglected in comparison with Q , V_g can be given by the relation:

$$V_g = \left[\frac{2J}{M} \frac{f_t}{F} \left(Q + \frac{1}{2} FRT \right) \right]^{\frac{1}{2}}. \quad (4)$$

Table (1) shows that the calculated values³⁾ of V_g agree with the observed values fairly well,

II. Effect of Diluent Gases on Detonation Velocity of $2\text{H}_2 + \text{O}_2$ Mixture

If excess of gases is added to the stoichiometric mixture of hydrogen and oxygen, a unit reaction may be expressed in the form



where X is the gas in excess, x its mole number and Q the heat of combustion.

Now it may be reasonable to consider that the heat of combustion is distributed equally among all the degree of freedom of reactant molecule (H_2O), but on collision of reactant with gas molecules in excess, the energy may be delivered mainly to the degree of freedom of translation of those excess molecules, for it has been known that on collision the probabilities of energy transfer into internal degree of freedom of molecules are far less than those for translation.⁷⁾⁸⁾⁹⁾ Accordingly, every polyatomic gas molecules in excess may act as monatomic in extremely short duration of collision.

Then the detonation velocity V will be given, as in the case of the preceding section, by the relation approximately

$$\frac{1}{2} M V^2 = J Q f_t / F^{**}, \quad (6)$$

where

$$M = \text{mass of } \text{H}_2\text{O} (M_{\text{H}_2\text{O}}) + \text{mass of } x\text{X} (xM_X),$$

* $F = f_r + f_v$ (rotation) + f_v (vibration).

** The last term of Eq. (3) in the preceding section is neglected.

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f_t = degree of freedom of translation in the unit reaction

$$\text{system} = f_{t\text{H}_2\text{O}} + x f_{t\text{X}'}$$

F = total degree of freedom in the unit reaction

$$\text{system} = F_{\text{H}_2\text{O}} + x f_{t\text{X}'}$$

and $f_{t\text{H}_2\text{O}} = f_{t\text{X}} = 3$; $F_{\text{H}_2\text{O}} = 12$; $M_{\text{H}_2\text{O}} = 18$.

For the stoichiometric mixture,

$$\frac{1}{2} M_{\text{H}_2\text{O}} V_0^2 = J Q f_{t\text{H}_2\text{O}} F_{\text{H}_2\text{O}} \quad , \quad (7)$$

where V_0 is the detonation velocity* in $(\text{H}_2 + \frac{1}{2}\text{O}_2)$.

From Eq. (6) and (7), we have

$$\frac{M}{M_{\text{H}_2\text{O}}} \frac{V^2}{V_0^2} = \frac{f_t}{f_{t\text{H}_2\text{O}}} \bigg/ \frac{F}{F_{\text{H}_2\text{O}}} \quad ,$$

or

Table 2. Effect of gases on detonation velocity in $(\text{H}_2 + \frac{1}{2}\text{O}_2)$ mixture.

X	xmols	V/V_0	Vcalc. m/sec.	Vobs. m/sec.	Vcalc. /Vobs.
O_2	0.5	0.8401	2363	2314	1.02
	1.5	0.7042	1985	1922	1.03
	2.5	0.6289	1772	1700	1.04
N_2	0.5	0.8660	2441	2407	1.01
	1.5	0.7385	2081	2055	1.01
	2.5	0.6637	1871	1822	1.03
H_2	1	1.200	3382	3273	1.03
	2	1.279	3605	3527	1.02
	3	1.309	3690	3532	1.05
He	0.75	1.124	3168	3010	1.05
	1.5	1.166	3282	3130	1.05
	2.5	1.176	3315	3160	1.05
A	0.75	0.744	2097	1950	1.08
	1.5	0.648	1826	1800	1.02
	2.5	0.573	1616	1700	0.95
2.82 He 1.18 A $M_X = 14.8^*$	2.0	0.870	2451	2390	1.03
1.5 He 1.5 A $M_X = 22^{**}$	2.0	0.801	2258	2830	0.97

$$* \quad M_X = \frac{4 \times 2.82 + 40 \times 1.18}{2.82 + 1.18} = 14.8 \quad .$$

$$** \quad M_X = \frac{4 \times 1.5 + 40 \times 1.5}{1.5 + 1.5} = 22.0 \quad .$$

* $V_0 = 2819$ (m/sec.)¹⁾

$$\frac{M_{\text{H}_2\text{O}} + xM_X}{M_{\text{H}_2\text{O}}} \cdot \frac{V^2}{V_0^2} = \frac{f_{t\text{H}_2\text{O}} + xf_{tX}}{f_{t\text{H}_2\text{O}}} \cdot \frac{F_{\text{H}_2\text{O}} + xf_{tX}}{F_{\text{H}_2\text{O}}}$$

Accordingly

$$V = \left\{ \frac{1+x}{(1+0.25)(x+M_X/18)} \right\}^{\frac{1}{2}} \times 2819 (\text{m/sec}). \quad (9)$$

Table 2. shows that calculated values of detonation velocities in various mixtures agree with the observed ones¹⁰⁾ fairly well.

III. Detonation Velocity of Solid Explosives

Denoting the propagation velocities of sonic wave in gas and liquid by U_g and U_l respectively, Kincaid and Eyring¹¹⁾ gave the following relation,

$$U_l = U_g(v/v_f)^{1/3}, \quad (10)$$

where v is the molecular of a liquid, and v_f its free volume.

In other words, sound wave in liquid can propagate in the free volume with the same velocity as in gas phase, and the time of propagation in the liquid molecules can be neglected.

Now, if it is considered that there are free volumes in the solid explosives on combustion and that the reaction velocity of the explosive molecules is infinitely large, the detonation velocity in the solid explosives (V_s) may be given analogously to the sonic wave by the relation

$$V_s = V_g(v/v_f)^{1/3}, \quad (11)$$

where V_g is defined by the relation (3) or (4) in Section I, and that can be calculated.

Neglecting the last term in the relation (3) in section I, Equation (11) becomes

$$V_s = (2JQ_T/M)^{1/2}(v/v_f)^{1/3}, \quad (12)$$

where $\gamma = f_t/F$. While, by the theory of liquid¹¹⁾,

$$(v/v_f)^{1/3} = L/2RT, \quad (13)$$

where L is the heat of evaporation and T is the absolute temperature of the liquid. According to Trouton's rule, we have

$$L/RT_b \cong 10, \quad (14)$$

where T_b is the boiling point of the liquid.

Accordingly, at T_b from Eq. (13) and (14) we have

$$(v/v_f)^{1/3} \cong 5. \quad (15)$$

Thus, the relation (12) becomes

$$V_s/(2JQ_T/M)^{1/2}=5. \quad (16)$$

Using observed values of V_s and calculated values of V_g , $(v/v_f)^{1/3}$ can be estimated as shown Table 3, where γ is assumed to be 0.24 from Table 1.

In Table 3, it is found that various kinds of solid explosives are classified as follows:

Group I	$(v/v_f)^{1/3} \cong 5$,
Group II	$(v/v_f)^{1/3} < 5$,
Group III	$(v/v_f)^{1/3} > 5$.

Table 3. Detonation velocities of solid explosives.

Group	Explosives	Charge density	Q/M Kcal/g	$V_s(\text{obs})^*$ m/sec.	$(v/v_f)^{1/3}$ $\gamma=0.24$
I	Cyan triazide	1.54	1.040	7500	5.2
	Picric acid	1.69	1.000	7260	5.1
	Hexanitro-diphenylamine	1.67	1.035	7150	5.0
	Dipentaerithrit hexanitrate	1.63	1.092	7400	5.0
	Pentaerithrit-tetranitrate	1.70	1.526	8700	5.0
	Nitroglycerine	1.60	1.485	8625	5.0
	Pentrit 80(11.5/8)0.5	1.72	1.480	8400	4.9
	Tetranitro-methane toluene	1.45	1.702	9000	4.9
	Trinitro-toluene	1.59	1.000	6870	4.9
	Tetranitro-methyl aniline	1.65	1.090	7250	4.9
	Tetranitro-benzene	1.63	1.065	7000	4.8
	Cyclomethylene-trinitroamine	1.70	1.500	8380	4.8
	Mannit-hexanitrate	1.70	1.454	8260	4.8
	Nitrogen-tetroxide-nitrobenzene	1.38	1.629	8500	4.7
	Nitro-cellulose	1.30	1.050	6800	4.7
	Dinitro-benzene	1.50	0.870	6100	4.6
	Glycol-dinitrate	1.50	1.665	8310	4.6
	Nitro-isobutyl-glycerine-trinitrate	1.68	1.597	8000	4.5
				mean	4.9
II	Explosive gelatine	1.63	1.610	7500	4.2
	Gelatine dynamite (65%)	1.60	1.295	6100	3.8
	Ammonium nitrate	1.10	0.350	2500	3.0
	Ammonium nitrate explosive (Donarit)	1.10	0.930	4000	2.9
	Explosive air (2.7% C 72.7 O ₂)	0.8	2.114	4700	2.3
	Nitroglycerine powder (48N _g /52N _e)	1.6	1.170	3000	2.0
	Chlorate explosive (Cheddit)	1.3	1.185	3000	2.0
	Ammonium perchlorate	1.2	0.312	1410	1.8
	Black powder	1.2	0.665	400	0.35
III	Lead azide	4.6	0.260	5300	7.3
	Mercuric fluminate	4.2	0.360	5400	6.4
	Lead trinitro-resorcinate	2.9	0.368	5200	6.1

* A. Stetbacher: "Schiess-und Sprengstoff," (1933), p. 62, 95.

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In the present theory, free volume has been assumed for solid explosives, while this assumption should essentially be applicable to liquids and Trouton's rule holds at their boiling points. Accordingly, the results shown in Table 3 suggest that those explosives in Group I at their flame fronts are approximately in the state of liquid at their boiling point, or that they have liquid structure essentially. This is reasonable, because most of them form molecular crystals. While, the explosives which belong to Group II are mixed powders or form ionic crystals, and there may be some difficulties in their liquefaction. Alternatively, it can be considered that, since explosives of Group II have relatively small charge density, apparent free volume or molecular gaps may be larger, and $(v/v_f)^{1/3}$ appears to become smaller. The explosives of Group III have larger charge density and apparent free volumes are smaller, and thus $(v/v_f)^{1/3}$ appears to be larger. Further, these last three explosives are detonators and have metallic atoms in their molecular structure. Such characteristics of their molecular structure may restrict the application of liquid theory to a considerable extent.

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